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Peroxychloroformyl Nitrate Synthesis and Thermal Stability

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16. ABSTRACT

Peroxychloroformyl nitrate, $ClC(O)OONO_2$, has been identified as the principal product of the ultraviolet irradiation of Cl_2, NO_2, and CO mixtures in air. Fourier Transform IR spectroscopic detection methods have been used to identify the newly detected compound and to establish its decomposition kinetics. The compound is at least as stable thermally as peroxy acetyl nitrate. It seems possible that peroxychloroformyl nitrate may have a role in stratospheric chemistry.

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Peroxychloroformyl nitrate, $ClC(O)OONO_2$, PClFN, has been identified as an oxidation product of chlorinated compounds and as the principal product of the ultraviolet irradiation of Cl_2, NO_2, and CO mixtures in air. Fourier transform IR spectroscopic detection methods have been used to identify this new compound and to establish its decomposition kinetics. The compound is at least as stable thermally as peroxyacetyl nitrate. PClFN is undoubtedly produced in the atmosphere where it most likely is a contributor to photochemical smog and possibly has some involvement in stratosperic chemistry.

1. Introduction

The gas phase synthesis of peroxynitric acid, $HOONO_2$, was recently reported [1,2]. Since then our laboratory has been engaged in the preparation of peroxyalkyl nitrates ($ROONO_2$) from various hydrocarbons [3]. In attempting to prepare halogen containing derivatives, peroxychloroformyl nitrate, $ClC(O)OONO_2$, (PClFN), was identified as an oxidation product of certain chlorinated compounds. We now show that the PClFN forms directly from the reaction of Cl, CO, NO_2, and O_2 and that the PClFN is at least as stable as peroxyacetyl nitrate (PAN).

2. Experimental

The synthesis and thermal decomposition studies of PClFN were carried out at 1 atm in a cylindrical Pyrex glass cell, 9 m in length by 0.3 m diameter and 700 ℓ in volume. The cell is evacuable and contains an eight-mirror optical system that allows in situ, infrared analysis of the reactants and products at a path of 216 m. The cell is surrounded by 96 fluorescent lamps consisting of 72 black-light lamps and 24 sunlight lamps. A detailed description of the cell and Fourier transform infrared system is given in other publications [3,4].

The reactant gases were of research grade (+99.0% minimum purity) and were used without further laboratory purification. Zero grade air containing less than 1.0 ppm total hydrocarbon was used as diluent gas.

3. Results

3.1. Synthesis

Peroxychloroformyl nitrate was originally identified as a stable oxidation product during the irradiation of 10 ppm of either methyl chloride or methylene chloride, 10 ppm chlorine, and 2 ppm of nitrogen dioxide in 1 atm of air [3]. In the present work, PClFN was directly synthesized by irradiation of 10 ppm of carbon monoxide, 50 ppm of chlorine, and 2 ppm of nitrogen dioxide in 1 atm of air. Absorption bands of PClFN are shown in the ratio plot (fig. 1). Also shown are absorption lines of HCl that is formed by the reaction of Cl atoms with methane impurity in the air. PClFN yields were obtained that were higher than 90% of the total possible yields, based on nitrogen balance.

3.2. Spectrum

Table 1 lists the principal absorption bands of PClFN and compares them with bands of peroxynitric acid, peroxyethyl nitrate, and peroxyacetyl nitrate. The ex-

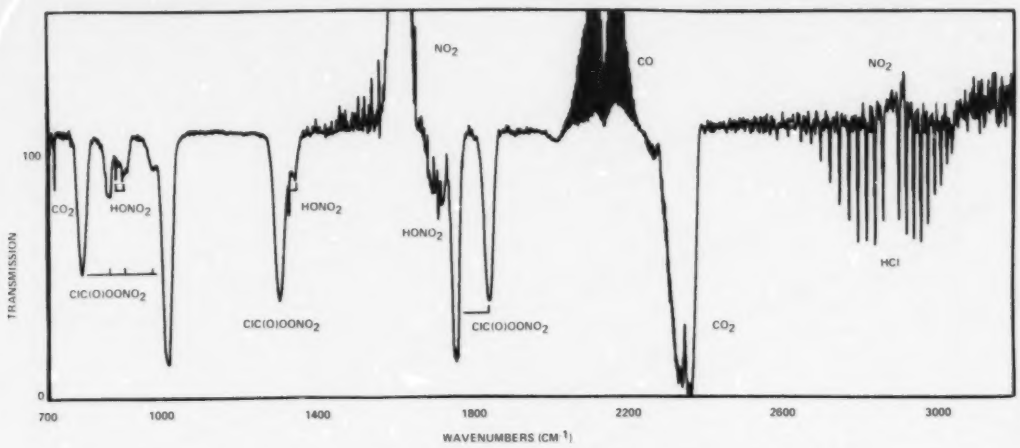

Fig. 1. Ratio plot: Spectrum of products divided by reactants. 10 ppm of carbon monoxide, 50 ppm of chlorine, and 2 ppm of nitrogen dioxide. Irradiated 10 min, optical path length 216 m, 760 torr pressure, resolution 2 cm^{-1}.

Table 1
Infrared absorption bands

Band centers for peroxynitric acid (cm^{-1}) [1]	Band centers for peroxyethyl nitrate (cm^{-1}) [3]	Band centers for peroxyacetyl nitrate (cm^{-1}) [5]	Band centers for peroxychloroformyl nitrate (cm^{-1})	k_ν for PClFN (atm^{-1} cm^{-1})
803	797	793	790	24
		1163	1015	65
1304	1298	1302	1300	28
1728	1720	1736	1756	73
		1838	1844	31

tinction coefficients, k_ν, quoted for PClFN were derived from mass balances of several irradiations. These values of k_ν, apply at the band maxima for the absorption equation $\ln(I_0/I) = k_\nu cl$, when the concentration, c, is in atmosphere and the path length, l, is in centimeter.

The table illustrates the similarity between the spectrum of PClFN and the spectrum of PAN. The three strong bands at approximately 800 cm^{-1}, 1300 cm^{-1}, and 1740 cm^{-1} are common to all peroxy nitrates and therefore may be assigned to vibrations in the peroxy nitrate functional group. The bands near 1840 cm^{-1} clearly are associated with the carbonyl functional group. The strong band at 1015 cm^{-1} in the spectrum of PClFN most likely results from a vibration involving the C–Cl bond.

3.3. Thermal stability

For the temperature dependence studies, 1 to 2 ppm of PClFN were prepared from CO in air at 700 torr. In order to prevent re-formation of PClFN after thermal decomposition, excess chlorine was used to convert carbon monoxide to carbon dioxide. Then, with the cell lights off, the total pressure was raised to 760 torr during the addition of 15 to 20 ppm of nitric oxide, NO, in nitrogen. The cell was heated to the desired temperature by means of the fluorescent lamps. NO was injected after the cell temperature had stabilized.

The decomposition of PClFN was observed by the decrease in intensity of the 1015 cm^{-1} absorption

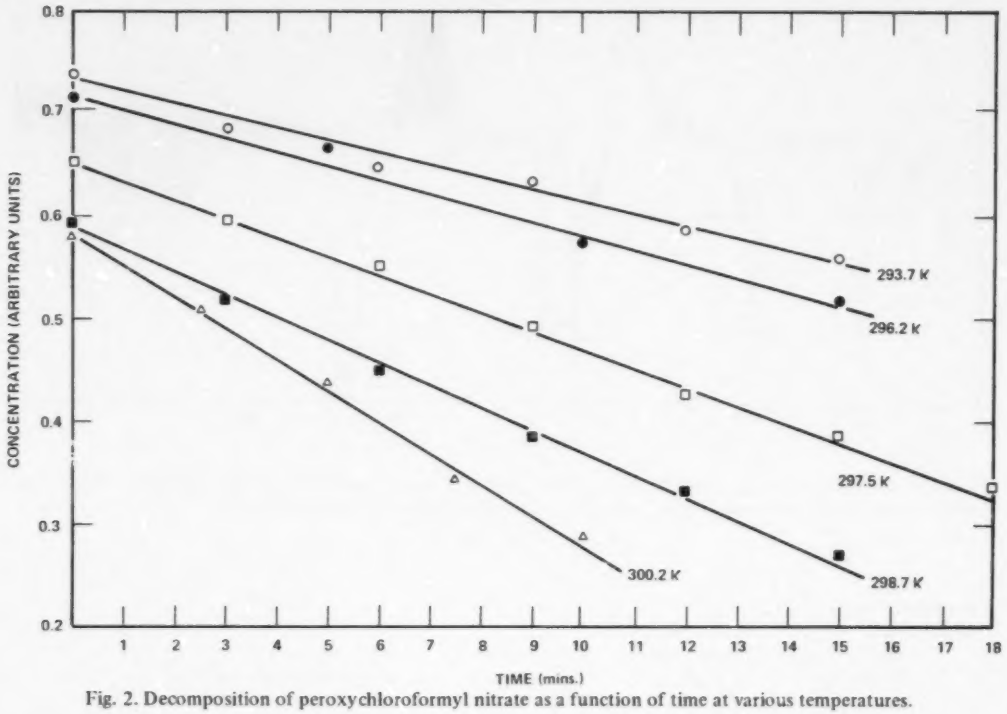

Fig. 2. Decomposition of peroxychloroformyl nitrate as a function of time at various temperatures.

band over a period of 15 to 20 min at 10 different temperatures. Plots of the decay of PClFN versus time at each temperature gave straight lines. Several of these plots are shown in fig. 2. Least-square regression analysis was used to determine the slopes of the decay lines. The values of the slope (k_{5a}) and the associated

Table 2
Rate and half-life data [a] for the decomposition of peroxychloroformyl nitrate in the presence of nitric oxide, as a function of temperature

T (K)	Rate constant $k_{5a} \times 10^2$ (min^{-1})	Coefficient of determination (R^2)	Half-life τ (min) [b]
293.7 ± 0.1	1.13 ± 0.14	0.943	61
295.0 ± 0.1	1.22 ± 0.15	0.938	57
296.2 ± 0.1	1.35 ± 0.15	0.976	51
296.8 ± 0.1	1.82 ± 0.08	0.992	38
297.5 ± 0.1	1.80 ± 0.05	0.997	39
298.4 ± 0.1	2.13 ± 0.05	0.998	33
298.7 ± 0.1	1.98 ± 0.05	0.998	35
299.2 ± 0.1	2.57 ± 0.08	0.996	27
300.0 ± 0.1	2.96 ± 0.06	0.998	24
300.2 ± 0.1	3.02 ± 0.10	0.996	22

[a] Data expressed at 1 standard deviation. [b] $\tau = 0.693$/rate constant.

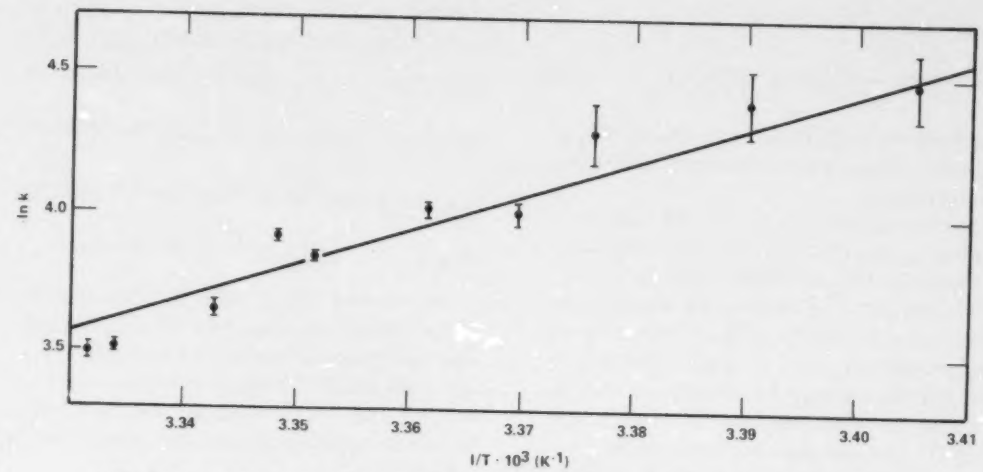

Fig. 3. Plot of $-\ln k$ versus $1/T$ for the thermal decomposition of peroxychloroformyl nitrate.

half-life are shown in table 2 as a function of temperature (K).

An Arrhenius plot of the thermal stability data (table 2) is shown in fig. 3. Least-square fit provides the following Arrhenius expression:

$$k_{5a} = 10^{18.6\pm1.6} e^{(-27.7\pm2.3\ \text{kcal/mole})/RT}\ \text{min}^{-1}. \quad (I)$$

This is the first order rate constant for the decomposition of PClFN in air at 1 atm pressure. The coefficient of determination is 0.9431 for this regression analysis.

4. Discussion

Chlorine atoms are first produced by photodissociation of chlorine; these atoms then react with carbon monoxide. The formation of the chloroformyl radicals, ClC(O), from the reaction of atomic chlorine and carbon monoxide and its associated equilibrium and rate constants have been studied by a number of investigators in oxygen-free systems [6,7]. The infrared spectrum of ClC(O) radicals has been recorded in matrix isolation studies [8].

$$Cl_2 + h\nu \rightarrow 2\,Cl, \quad (1)$$

$$Cl + CO + M \rightarrow ClC(O) + M. \quad (2)$$

Since our photooxidation study was conducted in the presence of oxygen, the chloroformyl radicals add oxygen, thereby forming the peroxychloroformyl radicals, ClC(O)OO. These radicals then react with nitrogen dioxide to form PClFN:

$$ClC(O) + O_2 \rightarrow ClC(O)OO, \quad (3)$$

$$ClC(O)OO + NO_2 \rightarrow ClC(O)OONO_2. \quad (4)$$

Peroxychloroformyl nitrate is the only chlorocarbon product observed (fig. 1) in our study. Atomic chlorine converts carbon monoxide to carbon dioxide, but this reaction does not become important until the nitrogen dioxide has been consumed. In earlier papers on the irradiation of chlorine, carbon monoxide, and oxygen mixtures, it was reported that carbon dioxide was formed by a chain reaction involving an oxygenated intermediate [9]. Our studies indicate that peroxychloroformyl radicals are the unidentified intermediate.

The decomposition rate of PClFN was measured as a function of temperature using an analysis similar to that employed by Cox et al. in the study of the stability of PAN [10]. It is assumed that PClFN dissociates and recombines via a mechanism described by the reaction

$$ClC(O)OONO_2 \underset{k_{5b}}{\overset{k_{5a}}{\rightleftharpoons}} ClC(O)OO + NO_2. \quad (5)$$

The introduction of NO destroys this equilibrium because of the oxidation of NO to NO_2 by the peroxy-

chloroformyl radical, ClC(O)OO,

$$ClC(O)OO + NO \xrightarrow{k_6} ClC(O)O + NO_2. \quad (6)$$

The recombination of ClC(O)OO radicals and NO_2 is thus prevented, permitting a measurement of the decomposition rate, k_{5a}.

The oxychloroformyl radicals, ClC(O)O, are unstable and decay into Cl atoms and CO_2. Infrared absorption bands for NO_2 (1600 and 2900 cm^{-1}) and for NOCl (1808 cm^{-1}) are observed for the decomposition products of PClFN. The NOCl is formed by the dark reaction (cell lamps off) of atomic chlorine with the added NO. Since a large concentration of CO_2 is present during the thermal decomposition study, small changes in CO_2 concentration are not detected.

The effective rate constant for the decomposition of PClFN is obtained by making the steady state approximation for the ClC(O)OO radicals:

$$d[ClC(O)OO]/dt = 0. \quad (II)$$

Using this approximation, one can show:

$$d[ClC(O)OONO_2]/dt = -k_{5a}^{eff}\,[ClC(O)OONO_2], \quad (III)$$

where

$$k_{5a}^{eff} = k_{5a}\left[1 - \frac{1}{1 + k_6[NO]/k_{5b}[NO_2]}\right]. \quad (IV)$$

Note that in the limit as the quantity $k_6[NO]/k_{5b}[NO_2] \gg 1$, we can neglect the second term in eq. (IV) and obtain $k_{5a}^{eff} \approx k_{5a}$ which gives simple-exponential decay for the solution of eq. (III):

$$\frac{[ClC(O)OONO_2]}{[ClC(O)OONO_2]_{initial}} = \exp(-k_{5a}t). \quad (V)$$

Because of the exponential decay, it is necessary to know only the relative concentrations rather than absolute ones. This avoids error due to the uncertainty of the absorptivities.

Increasing amounts of added NO were used until it was found that the decay rate was independent of the $[NO]/[NO_2]$ ratio. Eq. (V) could then be used for the analyses. Of course, by doing this, we lose information concerning the relative rates at which NO_2 and NO react with the peroxy radicals (k_6/k_{5b}).

The first order rate constant for the decomposition of PClFN is compared with those reported for peroxyacetyl nitrate, PAN, and peroxynitric acid, $HOONO_2$.

PAN [11] $k(T) = 10^{16.3}\, e^{(-26.9\ kcal/mole)/RT_s - 1}$,

PAN [10] $k(T) = 10^{14.9}\, e^{(-24.9\ kcal/mole)/RT_s - 1}$,

$HOONO_2$ [12] $k(T) = 10^{14.1}\, e^{(-20.7\ kcal/mole)/RT_s - 1}$,

PClFN $k(T) = 10^{16.8}\, e^{(-27.7\ kcal/mole)/RT_s - 1}$.

At a temperature of 298 K, the half-life of PAN is 26 and 30 min respectively for the two first order rate equations; peroxynitric acid is 8 s; and PClFN is 37 min. PAN and PClFN appear to fall into a common stability class. The data indicate that, if PClFN were formed in the ambient atmosphere it would be as stable as PAN.

Since PClFN can be formed from the stratospheric constituents carbon monoxide, atomic chlorine, and nitrogen dioxide, one may speculate that PClFN is also a constituent of the stratosphere. The PClFN molecule would have an effect similar to the chlorine nitrate molecules, $ClONO_2$, in removing chlorine atoms and nitrogen dioxide molecules from stratospheric interaction with ozone. The amounts of Cl and NO_2 that can be tied up in PClFN depend on the relative rates of the $Cl-CH_4$ nad Cl–CO reactions under stratospheric conditions, and on the amounts of available NO_2. These rates and amounts are not well known, but the limited available rate data indicate that the $Cl-CH_4$ reaction will predominate and the involvement of PClFN in stratospheric chemistry will be minor.

Perhaps the most important environment impact of PClFN will be found in polluted regions of the lower atmosphere. The degradation of chlorocarbons almost always proceeds through formyl chloride, HC(O)Cl, and/or chloroformyl radicals, Cl–C(O). If this degradation takes place in air that also contains NO_2, PClFN will be produced. Further studies are required on the formation and decay kinetics of PClFN and on its physiological and biological effects.

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